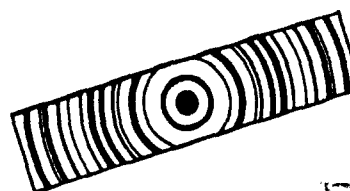
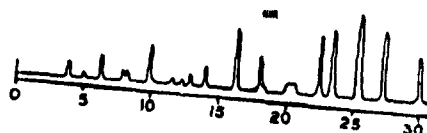
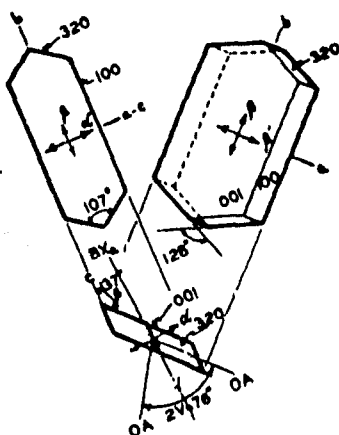
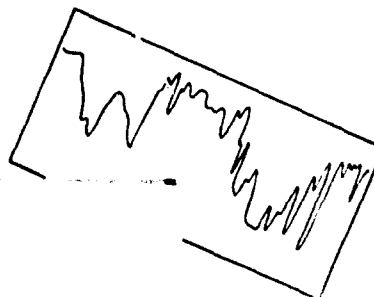
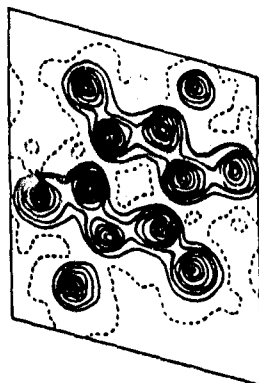


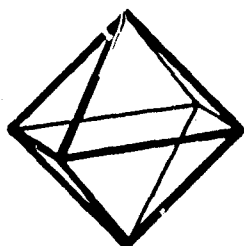
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To  
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Picatinny Arsenal  
Dover, New Jersey

FINAL REPORT  
ON  
THE CRYSTALLOGRAPHY OF EXPLOSIVES

Phase I Crystal Strain in Lead Azide  
Phase II Crystal Structure Determination  
by Polarized Infrared Absorption

Contract No. DA-11-022-ORD-4090  
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January 10, 1963

WALTER C. MCCRONE ASSOCIATES

# THE CRYSTALLOGRAPHY OF EXPLOSIVES

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# THE CRYSTALLOGRAPHY OF EXPLOSIVES

## Phase I Crystal Strain in Lead Azide

### I. INTRODUCTION

An additional year of effort has been completed in a program devoted in part to elucidation of the role of crystal lattice strain in the sensitivity behavior of lead azide. During the past year considerable additional experimental evidence continued to pile up but no unequivocal measure of lattice strain is yet available and consequently no graph has yet been drawn relating lattice strain to impact sensitivity.

The hypothesis that lattice strain energy increases the sensitivity of lead azide and that spontaneous detonation is due to sudden release of excessive lattice strain energy is no longer based solely on intuition. On many occasions growing crystals of  $\alpha$ -PbN<sub>6</sub> have been detonated by very gentle manipulation using a sharpened soft wood point to move the individual crystals by sliding in order to avoid intergrowths of two crystals growing too close together. The work done on such crystals is modest in the extreme. Generally there is no apparent resistance to the movement of the wood tip yet there is no question but that the action of the tip in sliding or tipping a 2 - 3 mm crystal under the aqueous growing solution has caused the detonation. One would have to estimate the force involved as perhaps just equal to the weight of the crystal or about 1 - 5 mg. (about 1 dyne).

As pointed out many single crystals have detonated while growing when "pushed" with a force of a very few dynes. That this is not a stilleto heel effect is proven by the shape and flexibility of the wood tip. The tip is large compared with the crystal and quite like a brush since the wood fibers become soft and frayed in the solution. Crystals grow in a similar manner but allowed to "anneal" without growth for a few hours either in the solution or dry can be crushed to an impalpable powder without detonation. In the impact machine a 500 gram weight must fall 20 - 30 cm. to be reasonably sure of achieving

detonation. Two crystals, apparently identical: one detonates with a 1 dyne gentle push; the other may not detonate with 500,000 dynes falling free from 20 cm. This is a fair difference in sensitivity associated only with crystal growth at the time of detonation or 12 hours standing since last crystal growth.

## II. OBJECTIVE OF THE RESEARCH PROGRAM

With increased confidence in the basic hypothesis that spontaneous detonation of  $\text{PbN}_6$  occurs as a result of excessive crystal lattice strain the objective of the program is now simply to measure lattice strain and sensitivity on a number of samples of  $\text{PbN}_6$  and to determine the relationship.

Two problems, aside from the major additional problem of controlled dependable growth of suitable crystals, can be formulated. One, a rapid quantitative measure of lattice strain and two, a rapid and dependable measure of sensitivity. Considering first, the measurement of strain energy one can outline a number of possible methods.

### Measurement of Crystal Lattice Strain.

1. Residual polarization colors at extinction. This method is difficult though non-destructive. It is orientation dependent and the strain birefringence is generally too low in small crystals to be measurable. Conversion of these measurements to an accurate measure of lattice strain itself is well-nigh impossible.

2. Cracking of the crystal due to strain. Crystals of  $\alpha\text{-PbN}_6$  often crack during crystal growth (with high linear growth rates; such cracking is less with low growth rates). There is no way of knowing whether cracking can trigger a spontaneous detonation. It may do so or both may be simply manifestations of crystal lattice strain. It might be possible to learn more about strain by measuring the mechanical properties of these crystals and thereby calculating the energy required to cause cracking.

3. X-ray diffraction effects. Effects of line or spot broadening undoubtedly exist as a result of lattice strain. No effort has been made with  $\alpha\text{-PbN}_6$  to observe any of these possible effects.

4. Differential thermal analysis. HMX has been observed to show a strain isotherm and this method was deemed worthy of trial during this year.

5. Melting point depression. Although lead azide cannot be melted the melting point of eutectics involving lead azide might be measurable. Since a strained crystal has a lowered melting point it is possible to measure the degree of lattice strain by the lowering of the melting point either of the pure material or of a eutectic involving that material (the ammonium acetate: lead azide eutectic immediately suggests itself).

6. Boiling point elevation. Strained crystals are more soluble than unstrained and saturated solutions in equilibrium with strained crystals would have a higher boiling point than the same solution in equilibrium with unstrained crystals. To use this procedure with lead azide would require a low boiling solvent to avoid loss of  $\text{HN}_3$ . A sealed system or reduced pressure might satisfy this requirement.

7. Osmotic pressure. Also a measure of solubility this method might be used in place of boiling elevation or melting point depression. A disadvantage might be the time required for equilibrium since we know that strain in lead azide anneals out in a few hours.

8. Direct solubility determination. The boiling point elevation and osmotic pressure measurements are indirect measures of solubility and have certain disadvantages. A unique method for the direct measurement of solubility is based on the use of the interference microscope. This microscope will measure the concentration of a solution in the neighborhood of a single crystal. This can be done at any temperature, crystal by crystal, and is both rapid and accurate. Furthermore, the changes in solubility as a function of time due to annealing can be followed, again, crystal by crystal.

9. Vapor pressure. Strained lead azide should have a higher vapor pressure however the vapor pressure of lead azide, strained or unstrained, should be extremely low. The flame ionization detector of the gas chromatograph might be sensitive enough.

10. Transition temperatures and rates. The transition temperature between  $\alpha$  and  $\beta$   $\text{PbN}_6$  is not known nor even whether it is above or below room temperature. In any case the transition temperature will change with strain in either form. The rate of transition at a given temperature will also depend on crystal lattice strain since the latter affects the

solubility which, in turn, controls the rate of transition.

11. Surface Etching. The nature of the lattice strain, whether deformation, defects, dislocations, or etc. will determine the rate and type of etch figures obtained on the surface of a dissolving crystal. The nature of the etched surface might correlate with the degree of strain.

Next, we should consider the possible methods for determining sensitivity preferably on single crystals of lead azide.

1. Standard Drop Test. This method is dependent on sample weight although the use of single crystals of small mass may be analogous to using an infinitely dilute solution in solution kinetics. Relatively large percentage differences in very small weights may have little effect. Otherwise this method is straight-forward and we already have an excellent impact sensitivity machine. If single crystals are used the orientation of the crystal may be important. An idea recently suggested by John Reffner and Dr. Azaroff sounds good in this connection. The single crystal would be surrounded by a liquid (no air bubbles present) and impact would be administered through a piston to the fluid and hence to the crystal.

2. Harvalik's Vacuum Drop Test. In this test the crystal itself is dropped in a vacuum through a long tube. The energy input is easily calculated although the point of impact on the crystal is not readily determined.

3. Shock Tube. Two parameters can be measured here: temperature of the shock wave and time delay before detonation. How either would behave relative to strain is not known nor whether either would be related to strain.

4. Ultrasonics. It would probably be difficult to be sure of good coupling unless as in 1. above, the crystals and transducer were placed in a liquid. Calculation of the energy input might be difficult.

5. Flash Tube. Energy input is easy to calculate on the basis of projected area and orientation effects can be studied.



6. Dielectric Heating. A pulsed H. F. oscillator may be used as energy input source. The energy input per crystal would, again, be very well known. This method would eliminate the effect of crystal orientation.

7. Hot Bar. One of the simplest heating procedures is to sprinkle a crystalline powder on a hot bar having a temperature gradient covering the explosion range. Single crystals can be placed on the bar at known temperatures and the time to detonation measured. Strained crystals should detonate sooner at a given temperature or conversely, at a lower temperature.

It is of the utmost importance to remember that the test used to measure strain or sensitivity must not change the degree of strain before the measurement is made. This would occur if strain is annealed out of the crystal during the experiment. Conversely, of course, the measurement method must not introduce strain. Since lead azide apparently anneals over a period of a few hours at room temperature any method for measurement of strain or sensitivity must be quick and since "annealing" probably occurs more rapidly at higher temperatures the method must take this into account. The methods chosen must measure strain and sensitivity of the same crystal or of comparable crystals without any change in strain or sensitivity before the measurement takes place. This is a stringent requirement. It would be possible under certain conditions of the experiment to alleviate all or a portion of the strain present before the measurement is made. Under other conditions the crystals could become strained or more strained during the measurement. Both situations must be avoided even though we don't know as yet just what conditions other than rapid growth rates cause strain in lead azide or the factors affecting the rate of annealing of any strain that may be present.

The research program which we are following is based on evaluation of the most promising methods of strain measurement and sensitivity determination. Most of the effort during the past year however has been exerted on additional proof that spontaneous detonation is due to lattice strain and on the major problem of growing good crystals of  $\alpha$ - $\text{PbN}_6$ .

### III. EXPERIMENTAL DETAILS

#### A. Methods of Growing Single Crystals of $\alpha$ -PbN<sub>6</sub>

Quarterly Progress Report No. 3 dated December 17, 1962 under this contract summarizes in detail the problems encountered during the past few years in attempting to grow perfect large crystals of  $\alpha$ -PbN<sub>6</sub>. After several years of extreme frustration and extremely slow progress a method and the necessary apparatus have now been developed and excellent crystals of any size up to 5 - 6 mm can be grown in about 2 weeks time. We have not yet attempted to make larger crystals but see no reason why, at least, 1 cm. crystals could not be grown.

The present method of growing crystals depends on diffusion of solute from a solution saturated at 36.5°C to a solution held at 30°C. The cooler solution then is supersaturated. Nucleation occurs spontaneously and growth of crystals occurs at a uniform rate of 0.2 - 0.3 mm/day depending on the number of crystals that nucleate in a given area. This growth rate although high for crystals several mm long seems so far to be safe. Since our safe growth rate data are based on temperatures around 20°C it is possible that PbN<sub>6</sub> can be grown more rapidly near 30°C. We have postulated before that PbN<sub>6</sub> should be grown very rapidly and very safely at higher temperatures where strain may not result during growth or, in a sense, be alleviated as rapidly as it forms. This should be tested one of these days by growing crystals with higher temperature gradients at higher temperatures (say 70°C and 55°C for the two liquid layers). Caution should be exercised here because we have observed spontaneous detonation at temperatures of 40, 42 (2), 43, 44, 45, 47, 50, 52 and 53°C.

The apparatus used for growth of  $\alpha$ -PbN<sub>6</sub>, shown in Figure 1, was described in detail in Quarterly Progress Report No. 3 dated December 17, 1962. It has continued to work reasonably well during the past few weeks and excellent crystals (Figure 2) are being grown routinely.

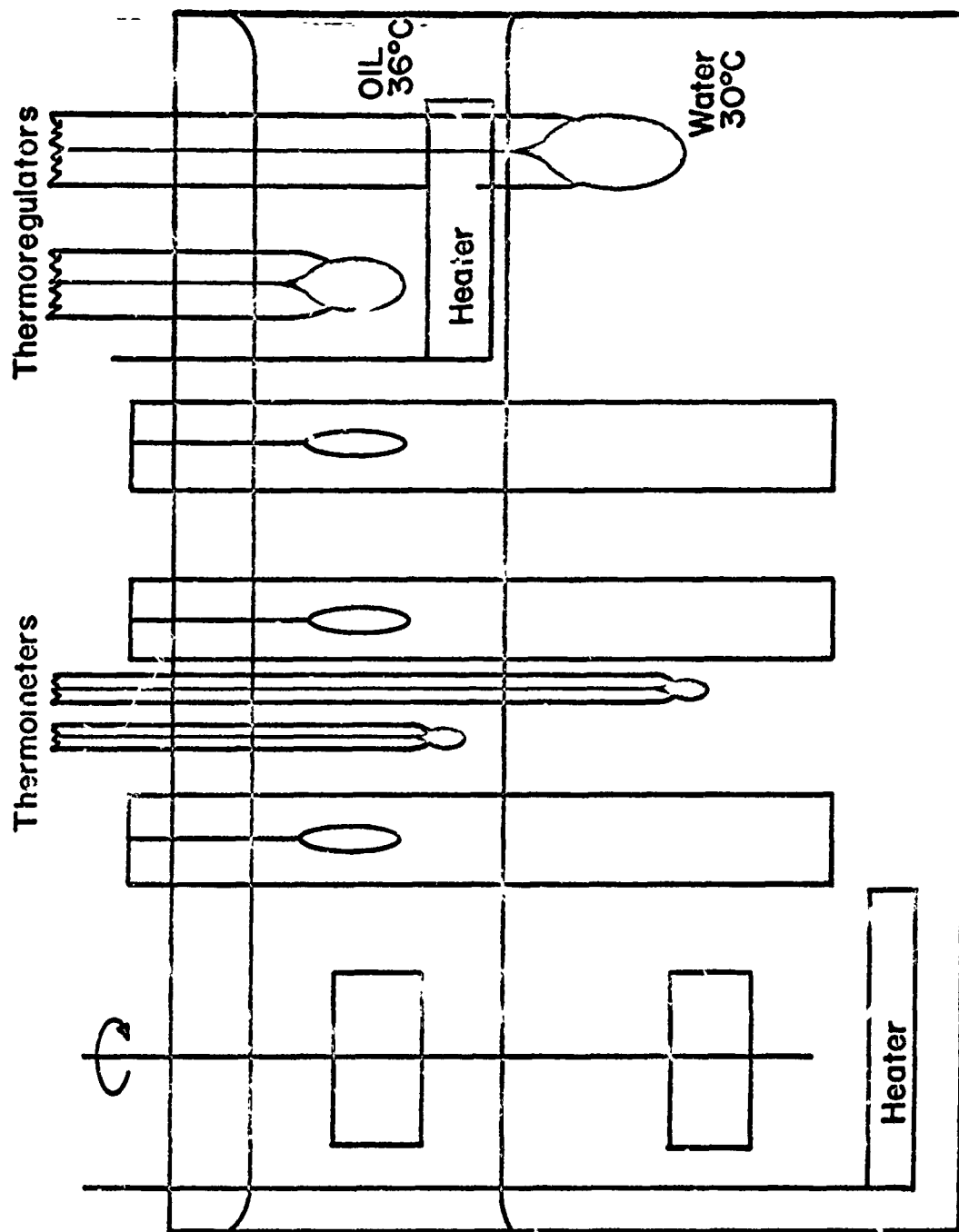


Figure 1  
Schematic view of bath for growing  $\alpha\text{PbN}_6$  single crystals



Figure 2. Photomicrograph of a 3+ mm crystal of  $\alpha$ -PbN<sub>6</sub> grown in the apparatus shown in Figure 1. The visible markings are all on the surface of the crystal and resulted from washing with water: a practice since abandoned.

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### B. Spontaneous Detonation of $\alpha$ -PbN<sub>6</sub>

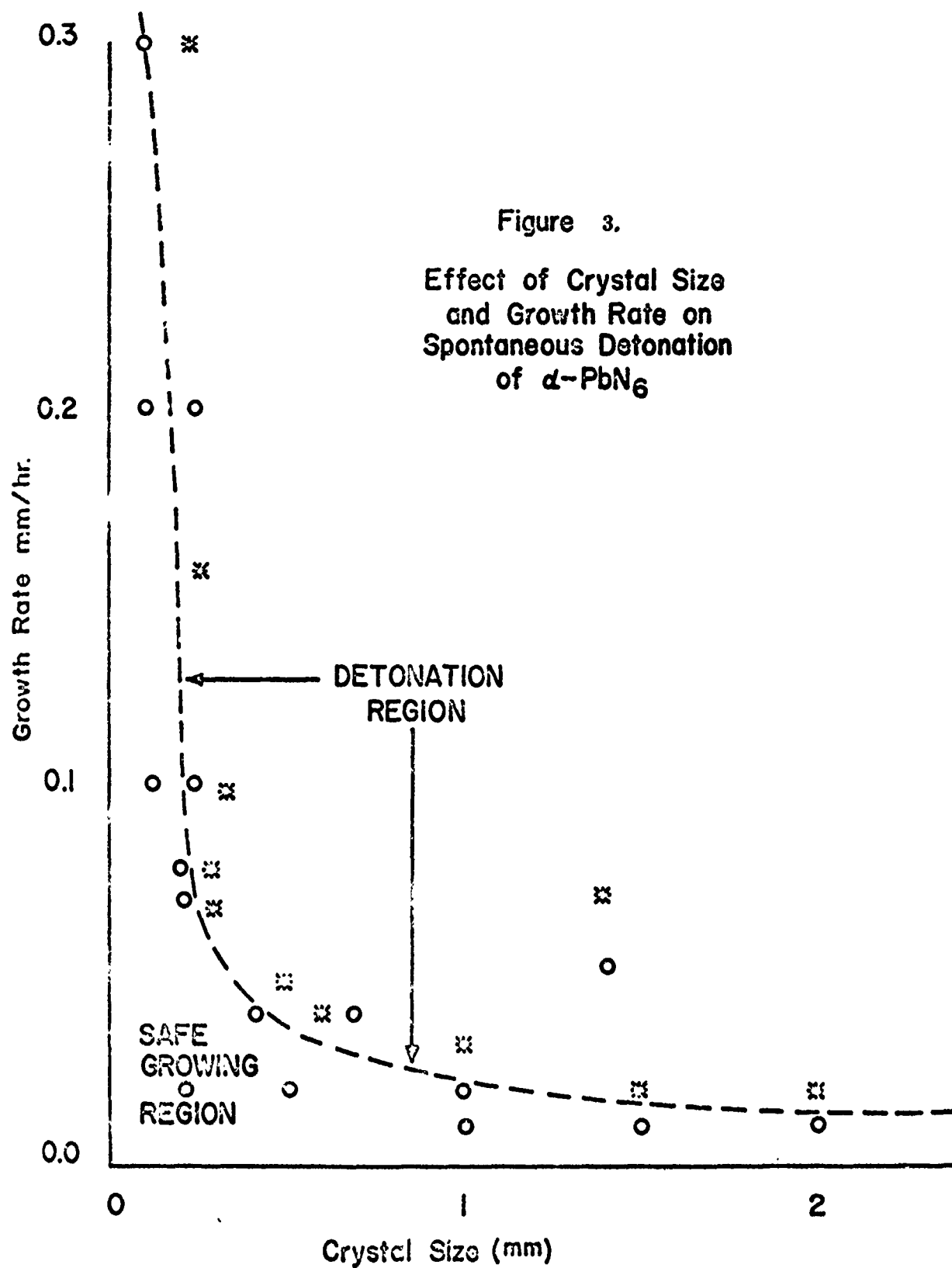
Figure 3 is a graphical summary of results covering spontaneous detonation of lead azide and the factors related thereto: crystal size and growth rate. It covers not only work done during the past year but many detonations from previous years where the necessary information was available. It represents far from a complete summary of spontaneous detonations since we have observed literally hundreds but in most cases we lack information on either the crystal size, the growth rate or both at the time of detonation.

### C. Impact Sensitivity of $\alpha$ -PbN<sub>6</sub>

Because of the lack of good crystals of PbN<sub>6</sub> until recently we have had no reason to develop a sensitivity method. Now, however, we do have good crystals and have ascertained the range of heights for a given weight of "ball" using our own impact machine (Figure 4). This machine was designed originally so that the weight could be changed by separating the vertical guides to accommodate steel balls of different diameters. Balls 2, 3 and 4 inches in diameter are available to us and the lightest of these weighs approximately 500g. The two heavier balls, weighing approximately 1.7 and 4.0 kg each, are much too heavy for PbN<sub>6</sub> and the smallest ball, weighing 500g, gives values of 50% point ranging from "zero" to about 20 cm.

To avoid the time delay in changing the impact machine back and forth for balls of different diameter we have decided to leave the machine set for the 2" ball which will take care of all common explosives except TNT and Explosive D. Since we are most interested in HMX, PETN, RDX and the azides we can encompass all of these by using the 2" diameter steel ball for the high explosives and a 2" diameter aluminum cylinder for PbN<sub>6</sub>. We can vary the weight of the aluminum weight by using 2" cylinders of varying lengths. A 1-1/2" length weighs about 200 grams giving a range up to about 50 cm for PbN<sub>6</sub>.

Considerable work is planned for the coming year on impact sensitivities. Since we do not as yet have an accurate measure of lattice strain the first approach will be to measure the sensitivity of freshly prepared PbN<sub>6</sub> immediately after crystal growth is stopped.



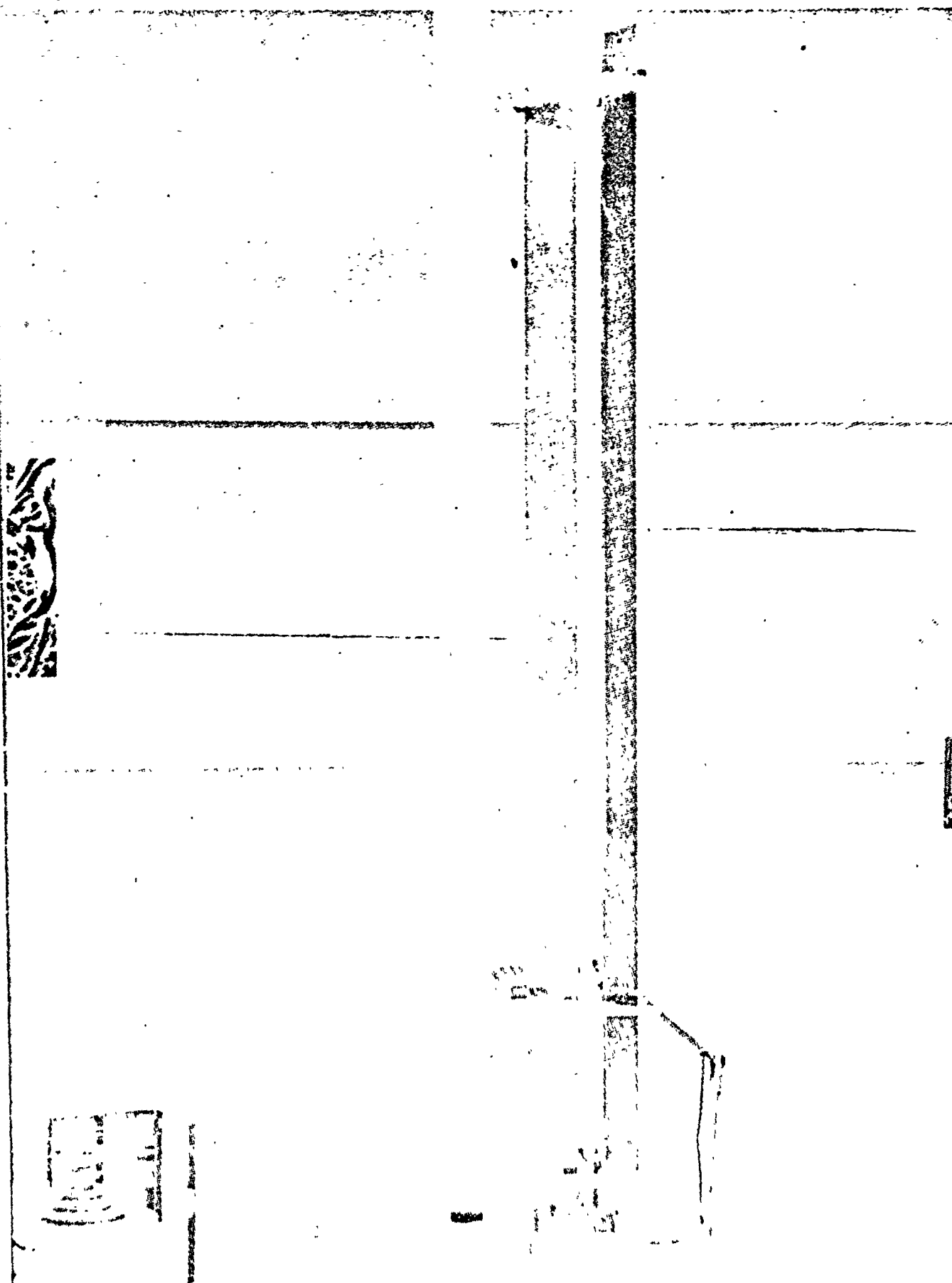
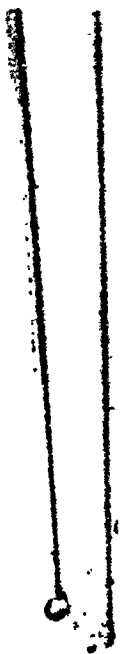
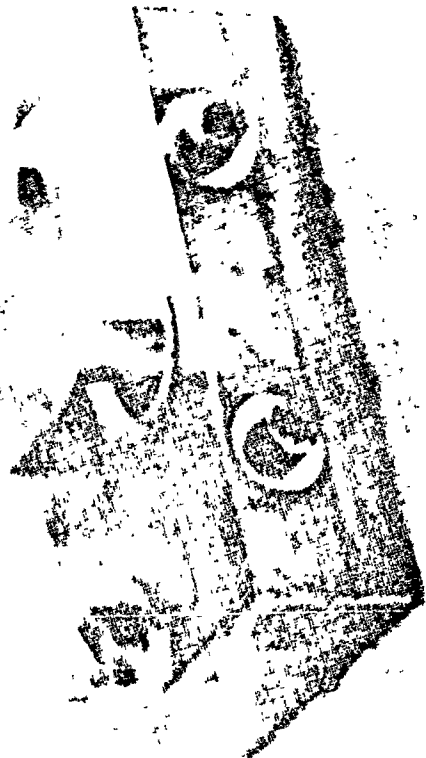
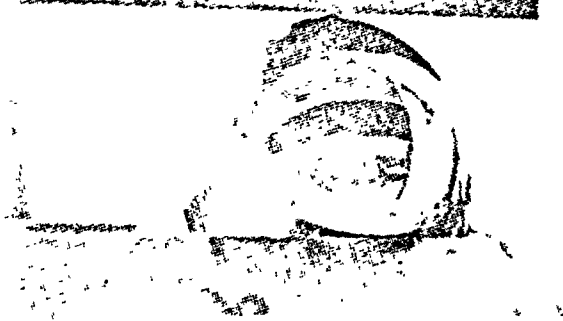
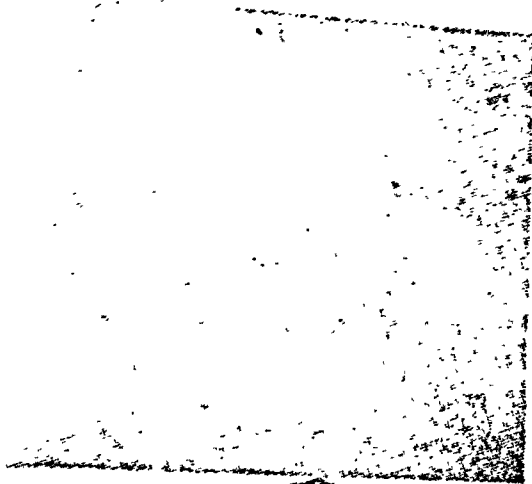


Figure 4. Impact sensitivity machine designed and built by McCrone Associates.

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Other portions of the same crystals will be tested from time to time thereafter. This will show for the first time higher measured impact sensitivity for freshly crystallized material as compared with annealed material. It will also give some idea as to the rates of annealing.

#### D. Differential Thermal Analysis

A considerable effort was made during the past year to determine what happens to  $\text{PbN}_3$  during heating and whether a strain isotherm can be found.

##### 1. Apparatus.

The DTA apparatus consists of temperature programmer, furnace, DC amplifier, potentiometer and two channel recorder. The furnace, (Figure 5), has a heater wound of No. 18 asbestos covered wire. The resistance would be one thousand watts when the voltage across the coil was 120 volts. This corresponds to the maximum power output of the temperature programmer. The resistances of the center and outside sections of the furnace were chosen so that the power transmitted per square inch would be the same in both sections. To reduce inductive effects of the heater coils in the furnace the wire was doubled before the winding was started. The metal used in the construction was steel which was machined so that the aluminum sample block was a close fit at room temperatures. The sample block is shown in Figure 6(top view only). It has two holes that hold the glass sample holders used in DTA and two pyrolysis cells which are covered with brass screw caps. Brass was used for these caps because aluminum caps were found to bind at the aluminum-aluminum interface of the threads after heating. It is not known whether or not this causes a temperature gradient in this region of the block.

In operation, the channels of the recorder were to be used to record the temperature difference between the inert and the sample and to record the temperature of the inert sample as measured by a second thermocouple. However, it was found that when the recorder was used for this purpose there was excessive noise and it was impossible to read the temperature by this method. An attempt was made to eliminate this noise by placing capacitors across the relays of the temperature programmer and by various grounding arrangements of the

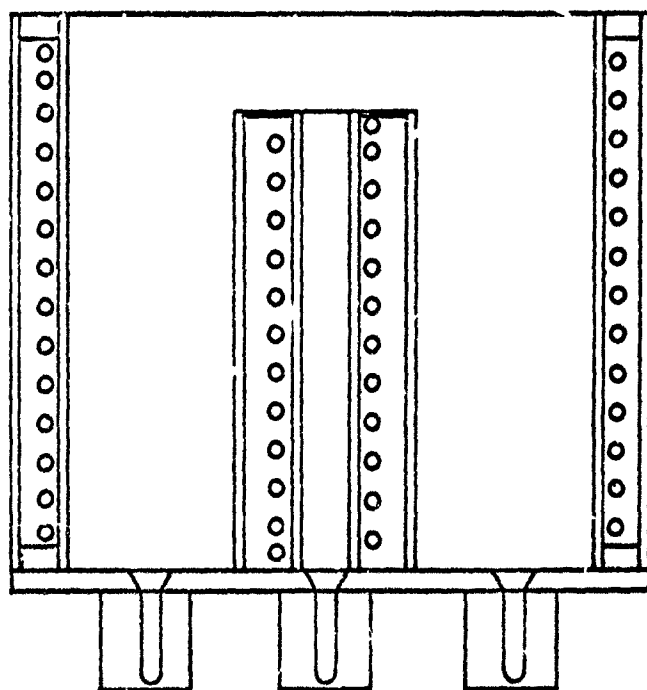
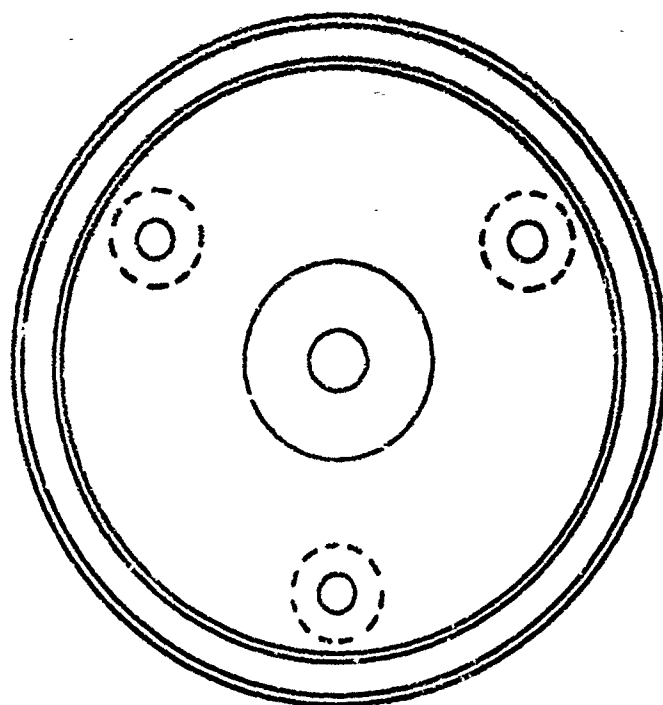


Figure 5. Furnace used as heater for DTA apparatus

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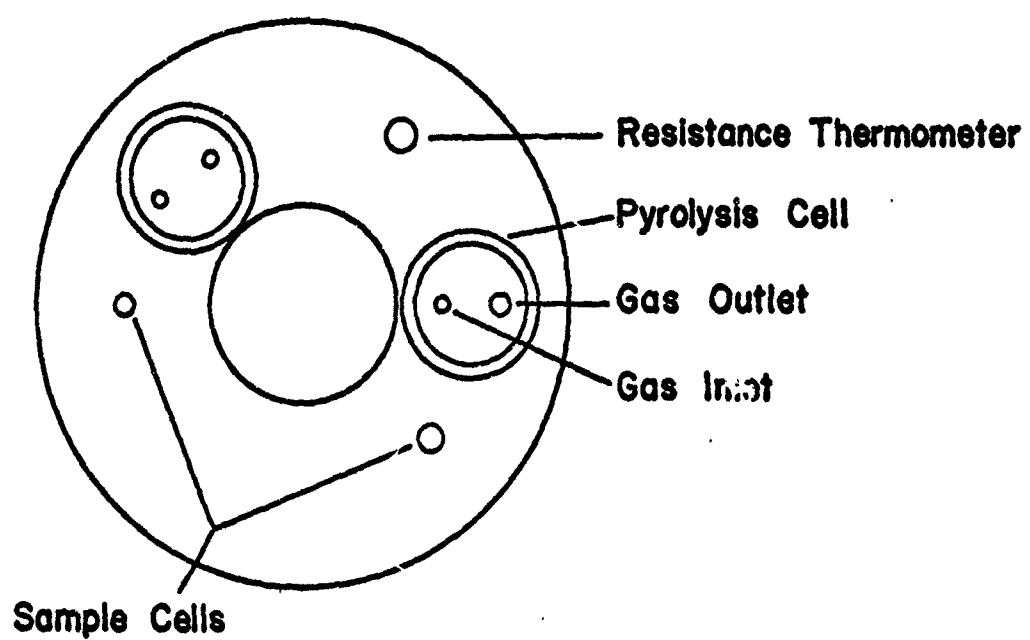


Figure 6. DTA Sample cell; fits into furnace shown in Figure 5.

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components. Although the noise was reduced, it was never reduced to the point where the recorder could be used to record the temperature of the inert sample accurately. At this point the arrangement was changed so that the output of this thermocouple was read by the potentiometer.

It was found that there would be a delay in the delivery of the thermistor thermoconductivity cell for the construction of the gas profile section of the DTA furnace hence it was decided to obtain gas profile data by using equipment not connected with the DTA apparatus. To do this, a Micro-Tek Gas Chromatograph was used. This is a dual column instrument with provisions for programming the column temperature to rise at a linear rate. The equipment was set up as for gas chromatography except that one column was replaced by a length of quarter inch copper tubing and the other column was replaced by the arrangement shown in Figure 7. A cross section of the sample containing section of this is shown in Figure 8. It consists of a quarter inch swagelok union into which is a hole bored in the nut part of the center section. A length of one-eighth inch copper tubing was silver soldered into this hole. The tubing was then attached to one quarter inch tubing which was connected by a fitting to the point to which the exit of the replaced column was attached. The carrier gas inlet to the replaced column is connected by one quarter inch tubing to one end of the union as shown in Figure 7. Two different sizes of sample holder were constructed from brass rod. A hole was bored in one end of a one quarter inch rod (3/4 inch long) into which fits the glass tube sample holders. It was then fitted with ferrules so that it could be attached to the end of the union with a gas tight seal. One of these holders takes the same size of glass tubing as is used for the DTA samples so that the data could be related since the two samples would have equivalent environments during heating. The system described above uses helium as a carrier gas and has a hot wire thermoconductivity detection system. When in operation, the detector block containing the hot wires is held above the final temperature of the column so that none of the evolved gases are allowed to condense before being detected. When the system was first placed in use there was some trouble with the temperature programmer not being linear but this has since been corrected.

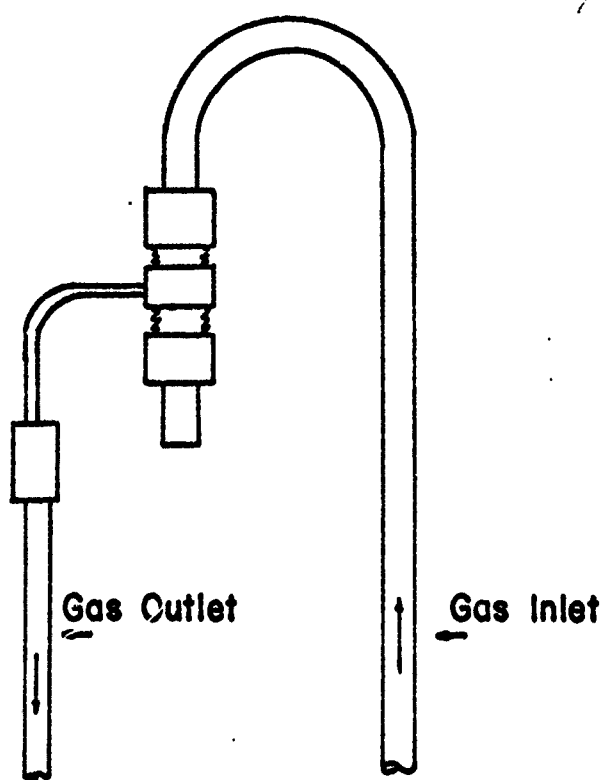


Figure 7. By-pass for the gas chromatography column to permit use of the instrument as a gas measuring device.

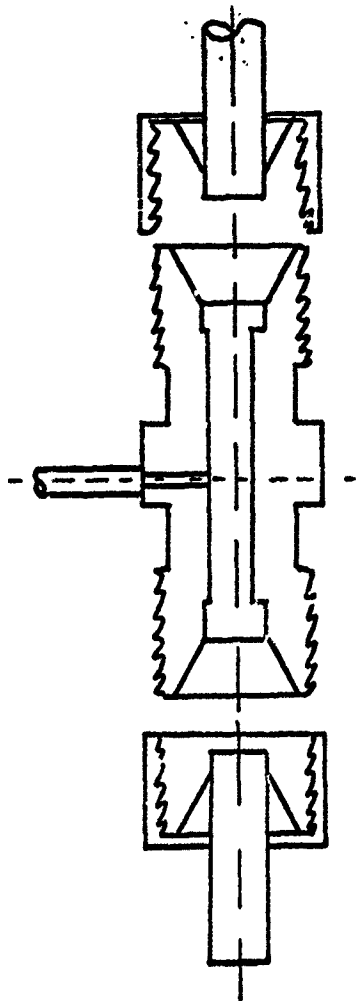


Figure 8. Sample holder for gas profile studies. Inserted in column by-pass but in furnace of gas chromatograph the temperature of the sample could be gradually increased and the volume of gas evolved measured.

The thermistor thermoconductivity cell arrived too late to be built into the DTA furnace, however it and a steel combustion tube are now on hand.

## 2. Procedure

The following is the procedure used in making a DTA run. The difference thermocouples, copper-constantan, are made with a common constantan wire. The junctions are welded in a gas flame. A known amount of the sample is then placed in a glass capillary and one of the difference thermocouples is then inserted into the sample and the capillary tube is placed in one of the holes in the sample block. The other thermocouple is then placed in the inert sample along with another copper-constantan thermocouple used for measuring the temperature of the inert sample. The output of the difference thermocouples is then soldered to the input of the DC amplifier and the thermocouple of the inert is connected to the potentiometer. These leads are lead out through a hole in the lid of the furnace. The recorder and DC amplifier are then turned on and allowed to warm up for about 30 minutes. The chart speed and voltage scale of the recorder are then set and the recorder is started. The zero is set at the desired point by using both the amplifier and the recorder zero adjustments. The recorder is returned to stand-by while the potentiometer is standardized and the required rate of temperature rise and the variac voltage are set on the programmer. The recorder is again turned on and either the inert sample or the test sample holder is warmed slightly by touching it and the resulting deflection is noted. This is done so that it will be known whether the deflections of the run are endotherms or exotherms. After the sample has cooled again the programmer is turned on. During the run the Variac voltage may be turned up if it seems that the temperature is lagging behind the programmed rate. The voltage of the inert sample thermocouple is recorded and at the same time the number of the readings is marked on the chart. After the run is over the corresponding temperature of the voltage is recorded.

The procedure used in the gas profile runs in the gas chromatograph is as follows. A sample of known weight is placed in one of the two sizes of glass sample holders available and the glass is then placed in the replaced column apparatus. The helium carrier gas is

turned on and a check is made to see if the system is gas tight by momentarily restricting the gas flow where it exits from the chromatograph. If the system is sealed, pressure will build up and there will be a noticeable noise when the restriction is removed. If this check is positive then the detector block heater is turned on and set for the temperature desired. After about five minutes the filaments of the detector are turned on and the current through them adjusted to approximately the desired current. Only after the detector block is at the desired temperature can the current be adjusted to its final value. At this point the equipment is allowed to warm up for at least three to four hours, or as long as it is necessary for the zero drift to minimize. Once this has been done the rate of temperature rise desired is dialed on the rate pot and the column heater is turned on. When this is done the temperature of the column will rise to the stand-by temperature as selected by the stand-by pot (lowest available 45°C) from which the program will start. The thermocouple located in the sample holder is connected to the potentiometer and the potentiometer is standardized. Once the program is started the output voltage of this thermocouple is recorded at intervals and at the same time noted on the chart.

Figure 9 shows the method used to determine the rate of temperature rise of the column. It is a plot of temperature vs. time on which the temperature was plotted every thirty seconds. The detector was on scale two in the above runs.

Figure 10 is a representative DTA run on  $\text{PbN}_6$ . The sample size was 7.6 mg. and the rate of temperature rise was 10°C/min. When the sample exploded it destroyed the sample holder and imbedded glass in the wall of the hole in the sample block making it impossible to use again without cleaning with a drill bit.

Figure 11 is the gas profile obtained from a run with 3.4 mg sample of  $\text{PbN}_6$ . The temperature rise rate is about eight degrees per minute. In this run the sample did not explode but decomposed slowly in contrast with the other runs made.

Figure 12 is the result of a run with a 5.3 mg sample of  $\text{PbN}_6$  whose temperature was raised at a rate of 10°C/min. The temperature at various points is marked on the plot. When this sample exploded it destroyed the glass sample holder. The large size glass tubing was used in all of the  $\text{PbN}_6$  gas profile studies because it was easier to load a sample.



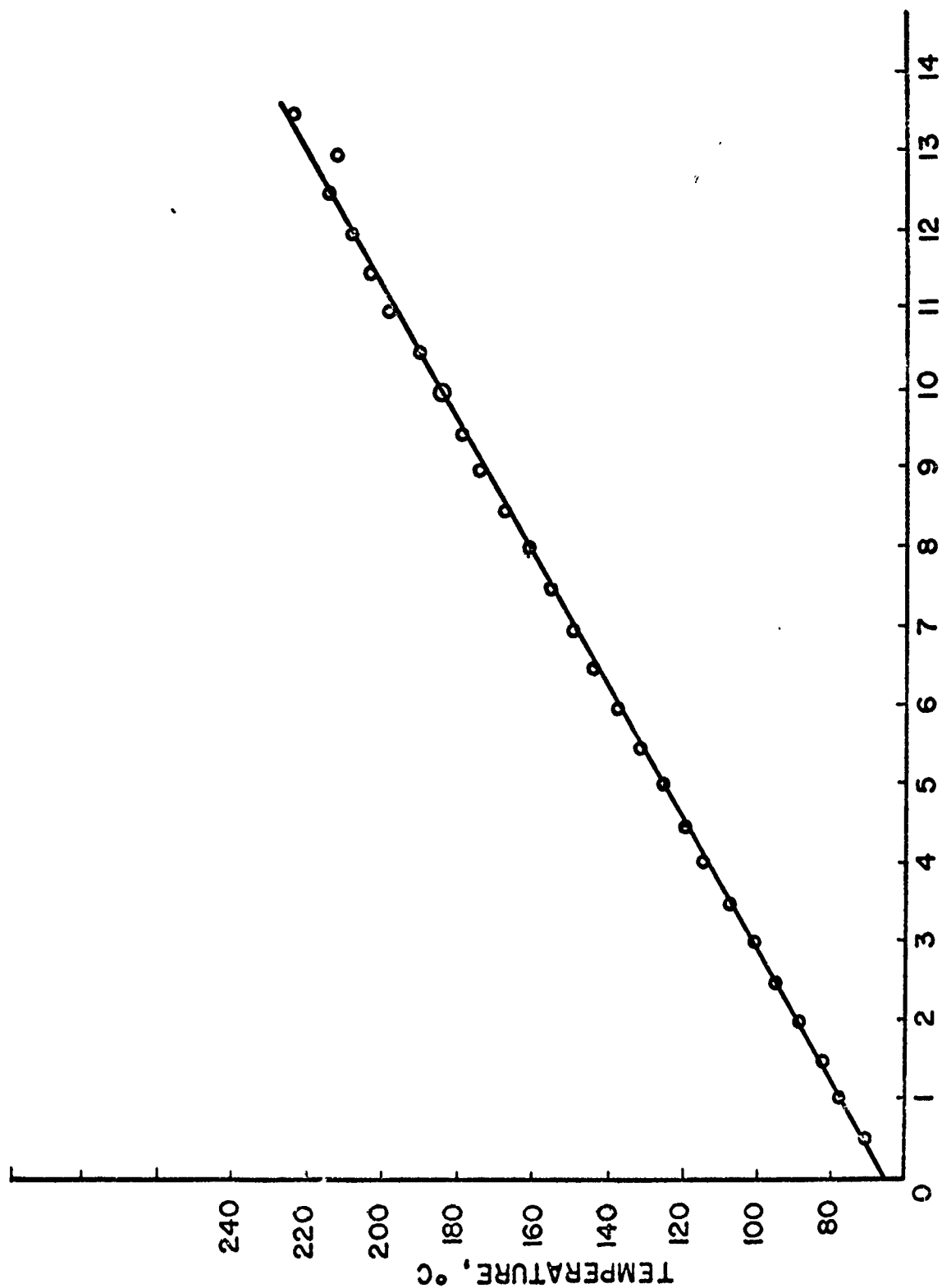


Figure 9. Heating rate of sample set for 11.5°C/min.

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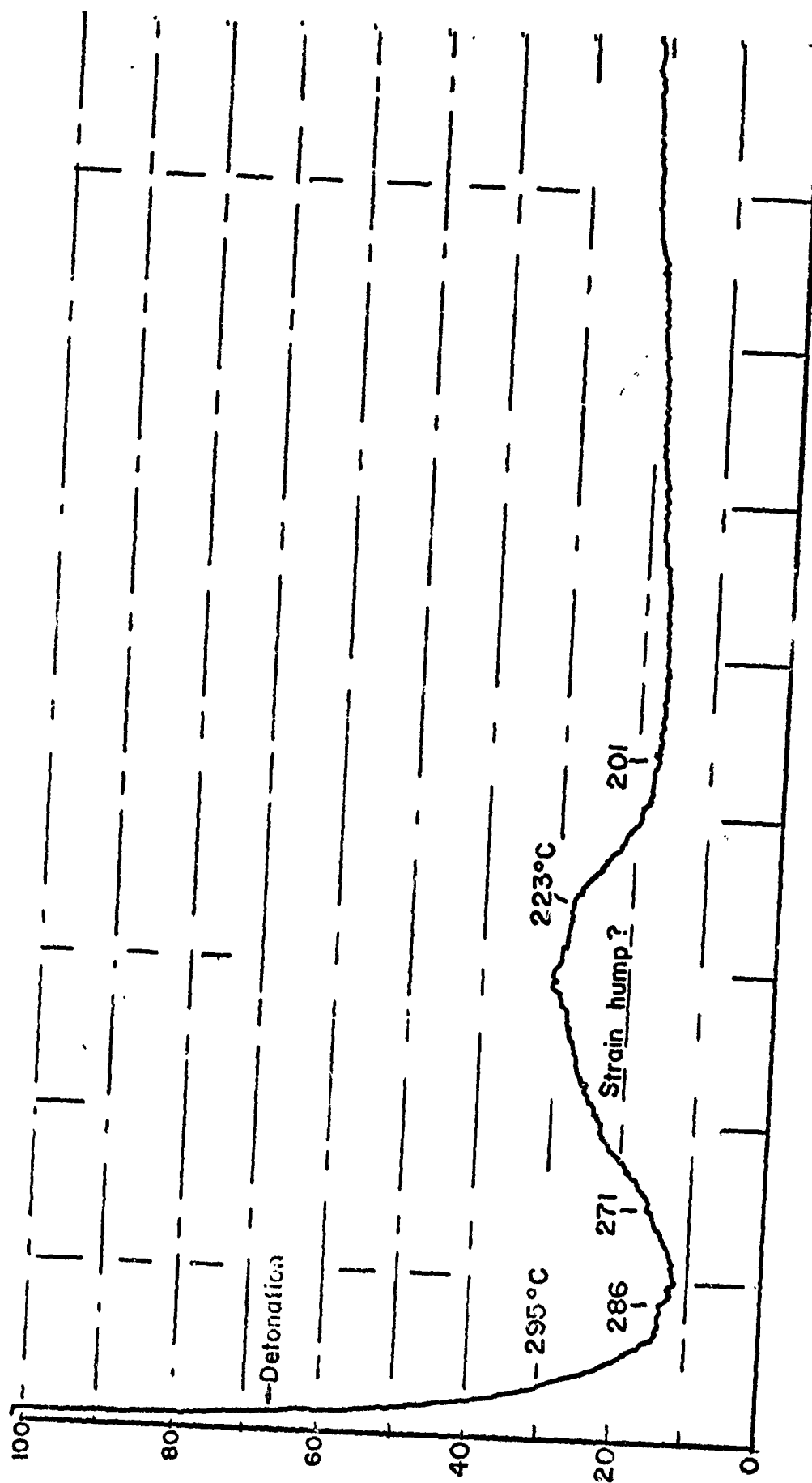


Figure 10. DTA run on 7.6 mg  $\alpha$ -PbN<sub>6</sub> heated 10°C/min.

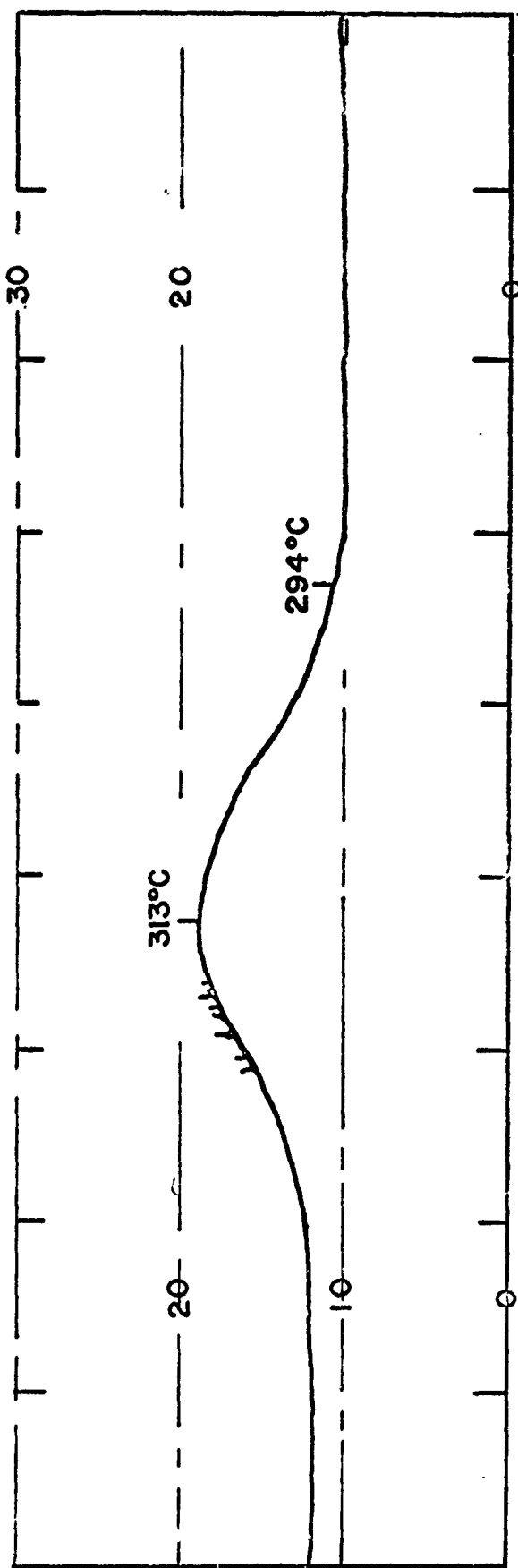


Figure 11. Gas profile run on 3.4 mg of  $\alpha$ -PbN<sub>6</sub> heated 8°C/min.

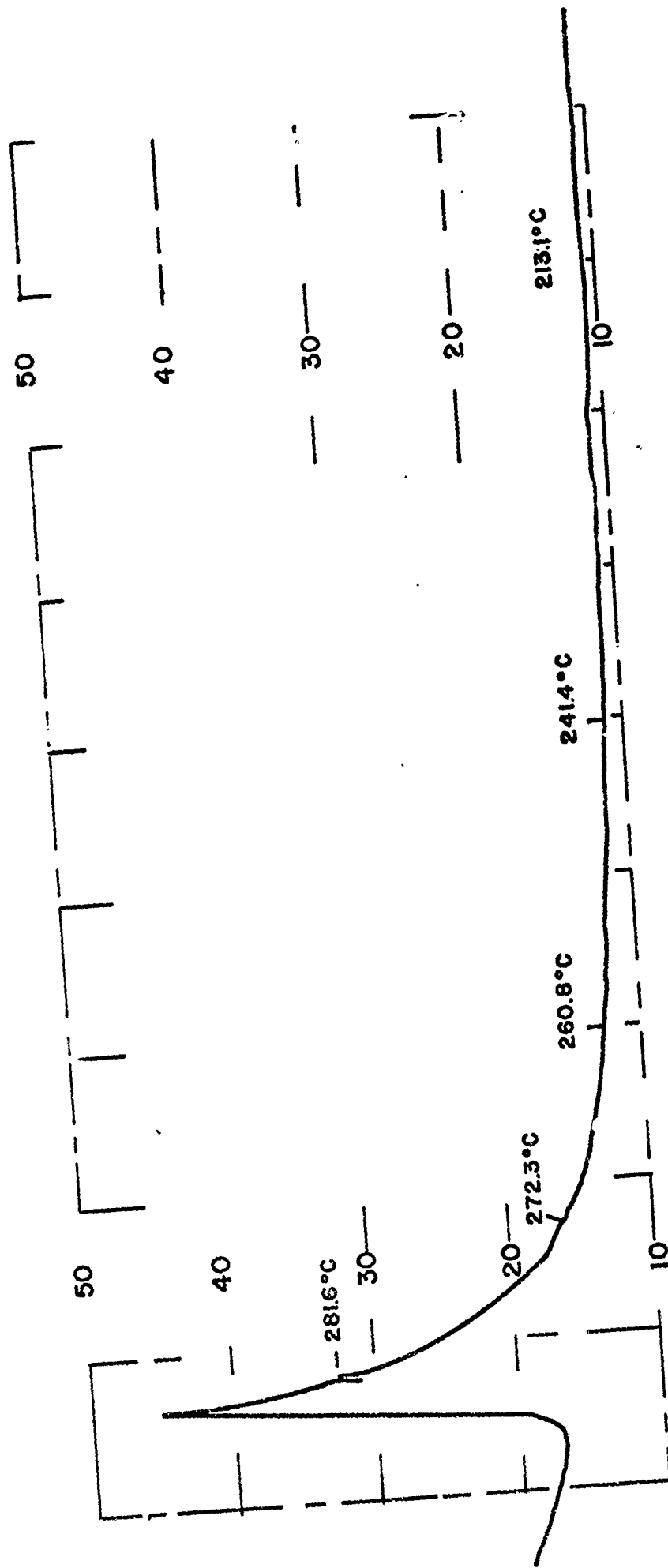


Figure 12. Gas profile run on 5.3 mg of  $\alpha$ -PbN<sub>6</sub> heated 10°C/min.

Figure 13 shows the results obtained from using 1.8 mg of  $\text{PbN}_6$  as a sample. The rate of temperature rise was  $28^\circ/\text{min}$ . The double peak structure shown here appeared in all of the runs where the sample exploded. The chart speed here was 20 seconds to the inch and in all other runs was one minute to the inch.

### 3. Conclusion

$\text{PbN}_6$  detonates when heated at rates as high as  $10^\circ\text{C}/\text{min}$ . but often survives when heated more slowly, even at  $8^\circ\text{C}/\text{min}$ . Detonation occurred at 285, 301 and  $335^\circ$  in different runs though all at  $10^\circ\text{C}/\text{min}$ . When detonation does not occur decomposition occurs slowly over a temperature range from  $290^\circ\text{C}$  to about  $335^\circ\text{C}$ . In the DTA curve there is an exotherm from about  $200^\circ\text{C}$  to about  $280^\circ\text{C}$  which is not associated with corresponding gas evolution. The cause of this exotherm is not known but because it is very broad and is not associated with gas evolution it cannot be a phase change since these changes are usually sharp and nearly always disrupt the lattice sufficiently to allow trapped gases to escape. This hump may well be due to annealing out of lattice strain.

We expect to pursue this possibility by checking other samples of  $\text{PbN}_6$  differing in the degree of strain, by rerunning a sample once heated to  $280^\circ\text{C}$ , etc. There is no problem involved in running very small samples, even including small single crystals weighing only 3 - 4 mg. but it is desirable to avoid detonation if possible because the destruction due to even such small samples is considerable even though confined to a very small volume.

### E. Nuclear Quadrupole Resonance

During the past year one of our consultants, Jack Dodd, suggested that nuclear magnetic resonance might be a useful technique for the study of strain in crystal lattices. Closely related to NMR, NQR is a quantity that characterizes the departure of the nuclear shape from sphericity. Since NQR requires no magnet suitable electronics can be assembled for a few hundred dollars in order to measure the shape of the nuclear quadrupole line and the relaxation processes. The shape of the NQ line depends on 1.) dipole-dipole interactions of adjacent nuclei, 2.) the presence of paramagnetic ions, 3.) spin lattice relaxation time and 4.) mechanical stresses.

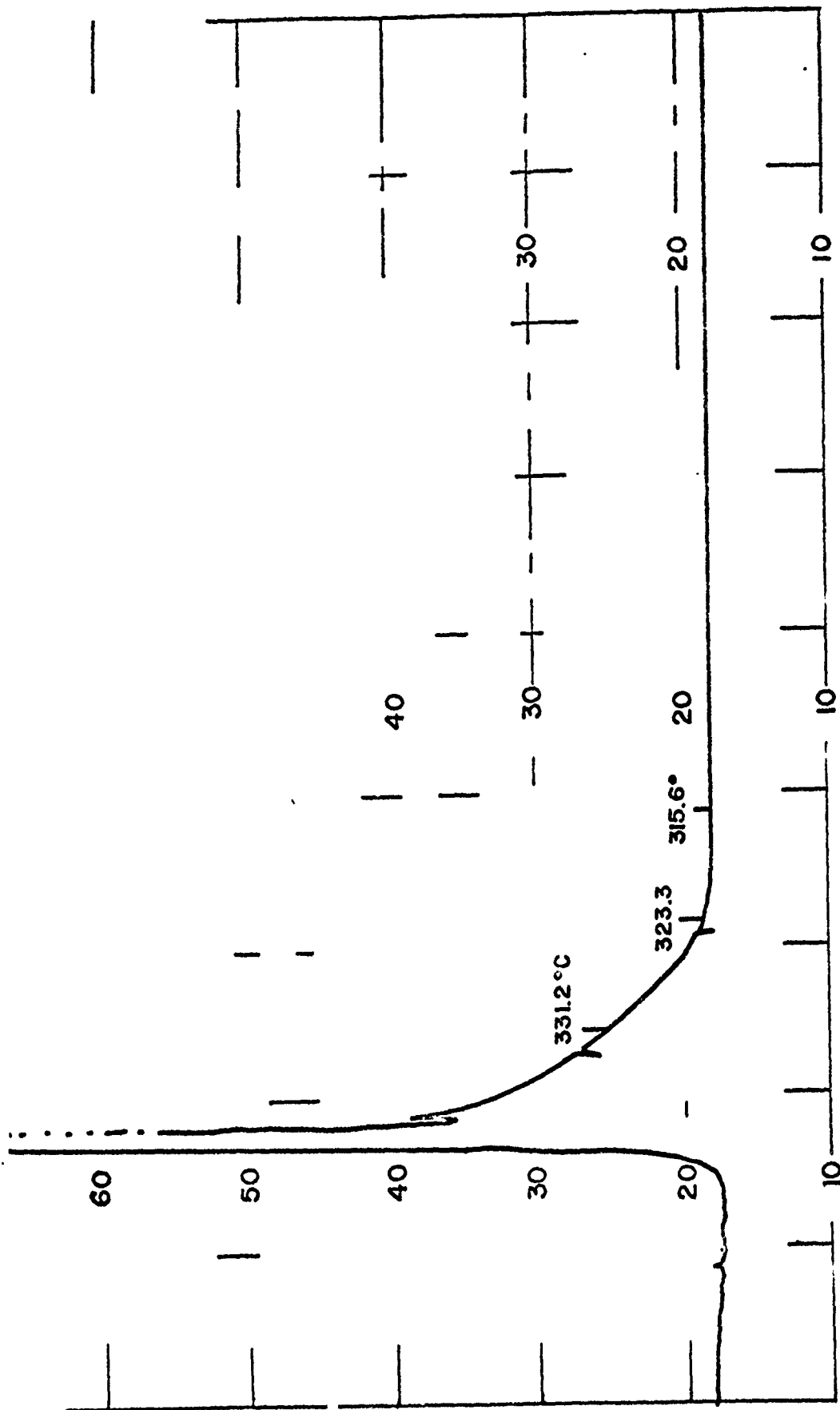


Figure 13. Gas profile run on 1.8 mg of  $\alpha$ -PbN<sub>6</sub> heated 28°C/min.

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Not only is it feasible to measure lattice strain but the orientation of the azide groups themselves in a single crystal should be evident. The latter is based on the orientation of the nitrogen nucleus in the divergent field of the lead nucleus. To determine the structure of  $\alpha$ - $\text{PbN}_6$  an external magnetic field of a few hundred gauss is used to split these resonances. The crystal is then rotated until the splitting is a maximum, in which position the azides are aligned with the magnetic field. There may of course be several such positions depending on the structure.

To determine lattice strain, one examines again the resonances since strain broadens these in a calculable manner.

The beauty of the method is the simplicity and low cost. The equipment needed for the study of the nitrogen nucleus is especially inexpensive since observations need be made over a probable range of only 3 - 5 megacycles. One requires:

- 1.) Oscillator detector, either super-regenerative, or marginal oscillator
- 2.) Oscilloscope
- 3.) Dewar
- 4.) Helmholtz coils and Power supply.

During the past few months a NQR apparatus has been quietly built and tested. A first test using hexamethylene tetramine was quite successful in giving a good set of resonances; however, no results have yet been obtained on other nitrogen containing compounds. HMX has been tried but the large sample size and the requirement of large crystal size has so far prevented experiments with  $\text{PbN}_6$ . Experiments with  $\text{KN}_3$  will be tried soon and the apparatus is now being modified to allow for the possibility of resonances below 3 megacycles. The possibility that the resonance relaxation times are too short for measurement is also being considered and a low temperature cell will be built to lengthen these times.

During the next year considerable additional work will be carried out with this apparatus or its lineal descendants.

## Phase II Crystal Structure Determination by Polarized Infrared Absorption

### I. INTRODUCTION

During the past several years a variety of attacks have been made on the crystal structures of the two crystal forms of  $\text{PbN}_6$ . Only partial success has been achieved; in part, due to the difficulty of growing suitable crystals and, in part, due to the considerable disparity in x-ray scattering power by lead and nitrogen atoms. The net result has been a pair of excellent structures for the lead only, in the  $\alpha$  and  $\beta$  polymorphs (Figures 14 and 15).

We suggested, as a result, the possibility of using polarized infrared absorption. When polarized infrared radiation falls on a crystal absorption may occur but only when the electric vector of the radiation is oriented at some angle different from  $90^\circ$  with the dipole moment of the absorbing chemical bond. By determining the orientation of a crystal where absorption is a maximum or a minimum the position of the absorbing chemical bond can be determined. A good example is the work done in this laboratory on TNT. Figure 16 shows the infrared absorption patterns for a parallel array of TNT crystals (essentially a single crystal of TNT) oriented in two mutually perpendicular orientations with respect to the plane of polarization of the incident light. These two directions, A-A and B-B, are as shown on a single crystal of TNT in Figure 17. The resulting orientation of the molecule of TNT is also shown in Figure 17 as derived from the infrared data.

Infrared spectra for azides have already been analyzed and azide assignments have been made (a strong bending mode at about  $642\text{ cm}^{-1}$  and a stronger stretching mode at about  $2030\text{ cm}^{-1}$ ). The extent to which these two absorption bands appear in polarized infrared spectra of a given azide crystal is determined by the orientation of the azide groups in those directions parallel to the vibration direction of the polarized light. It may even be possible to make this determination quantitative by determining the specific



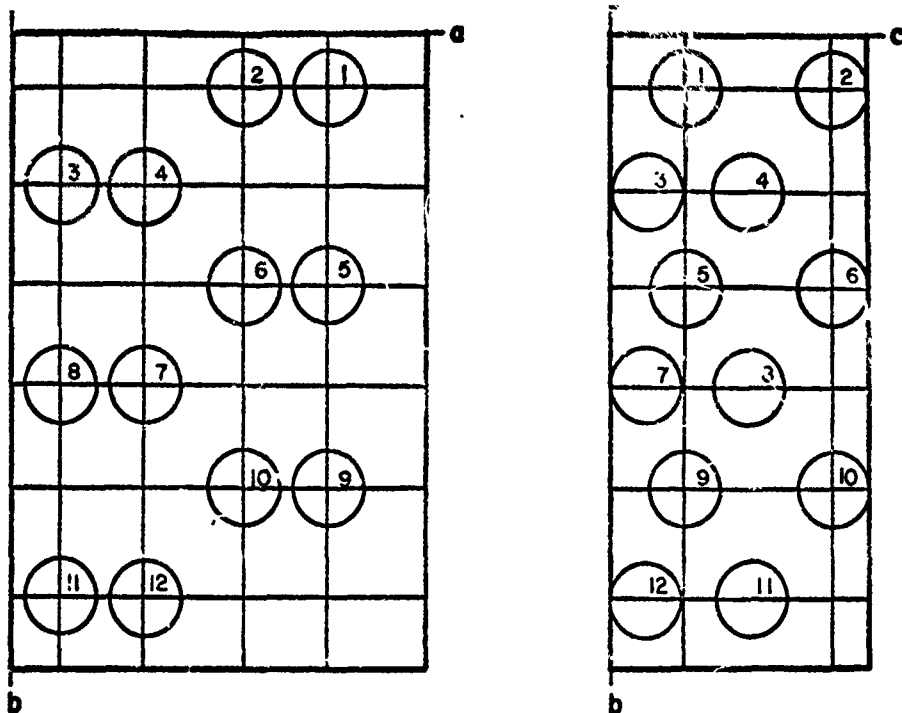


Figure 14. a-b and b-c projections of alpha lead azide showing the positions of the 12 lead atoms (identical numbers indicate same atoms). This same cell contains 24 azide groups or 72 nitrogen atoms.

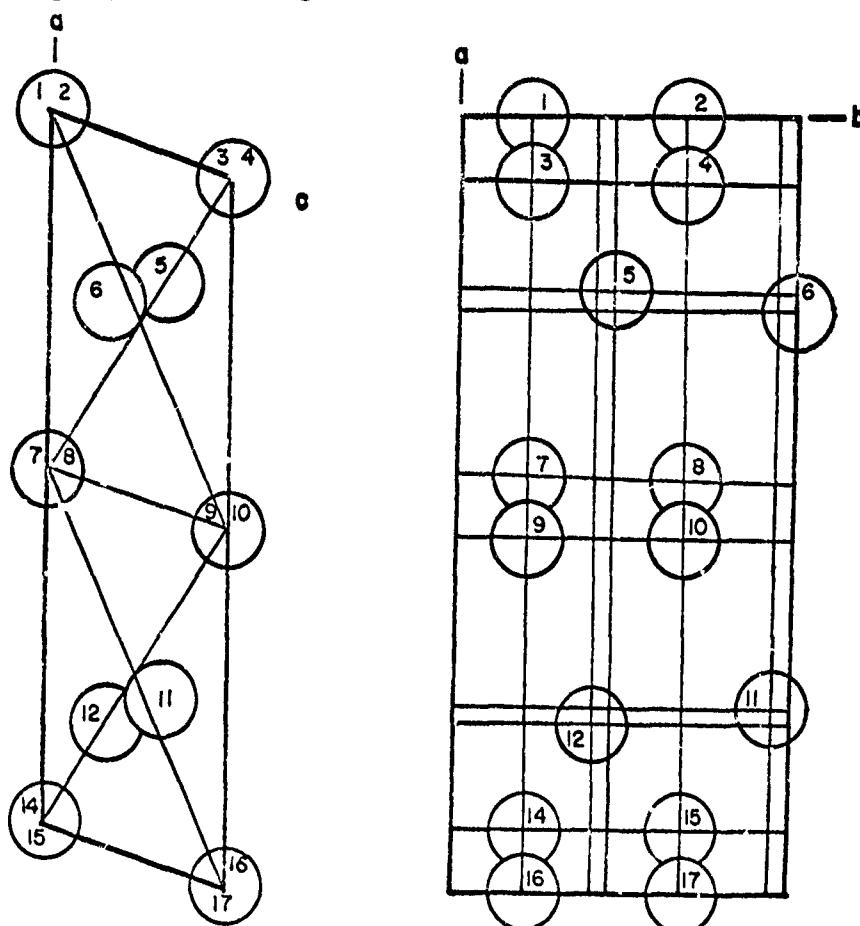


Figure 15. a-c and a-b projections of beta lead azide showing the positions of the 8 lead atoms plus several additional lead atoms to make the structure clearer (identical numbers indicate same atoms). This cell will also contain 16 azide or 48 nitrogen atoms.

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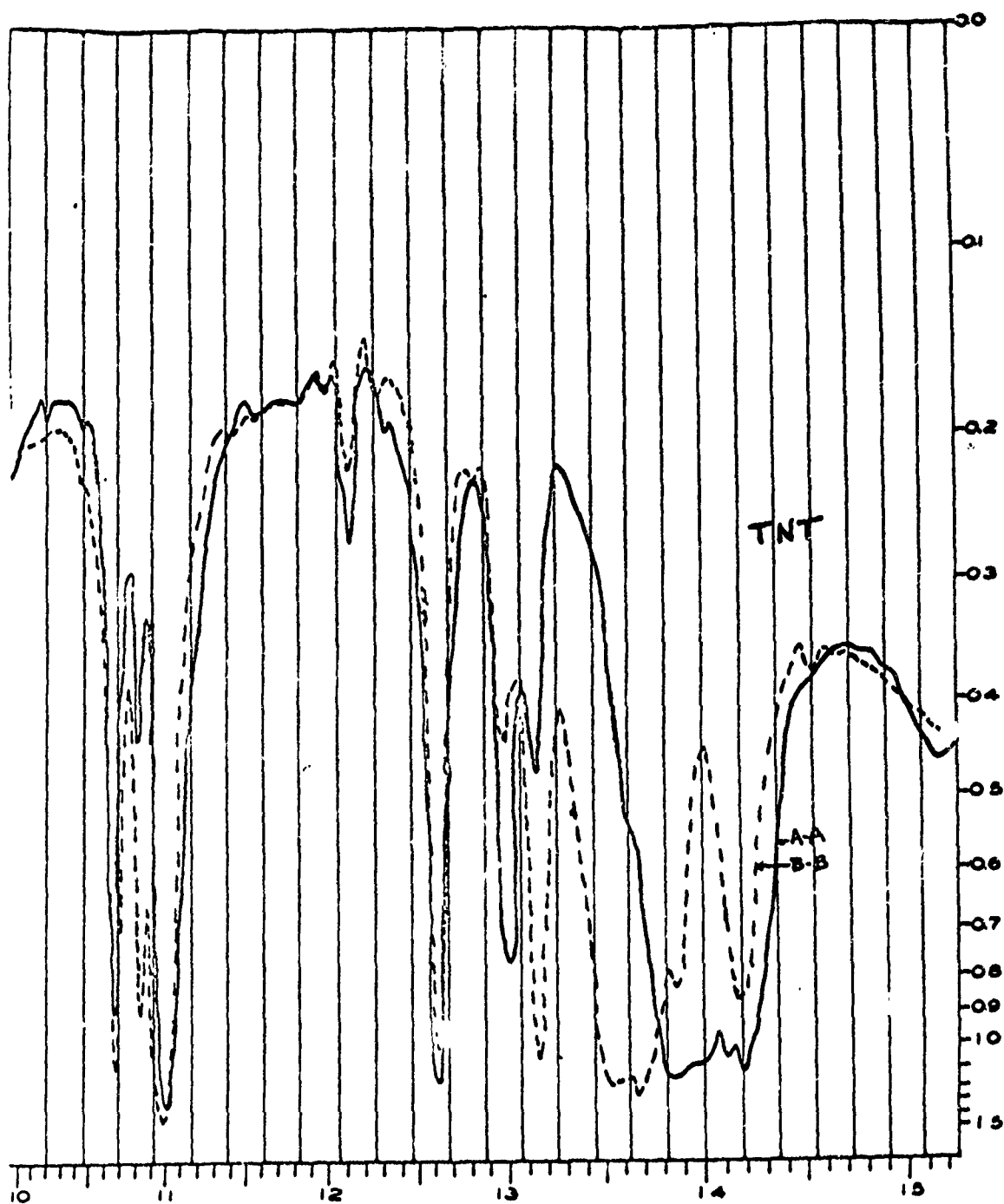


Figure 16, Polarized infrared absorption patterns for two different directions in parallel array of TNT crystals.

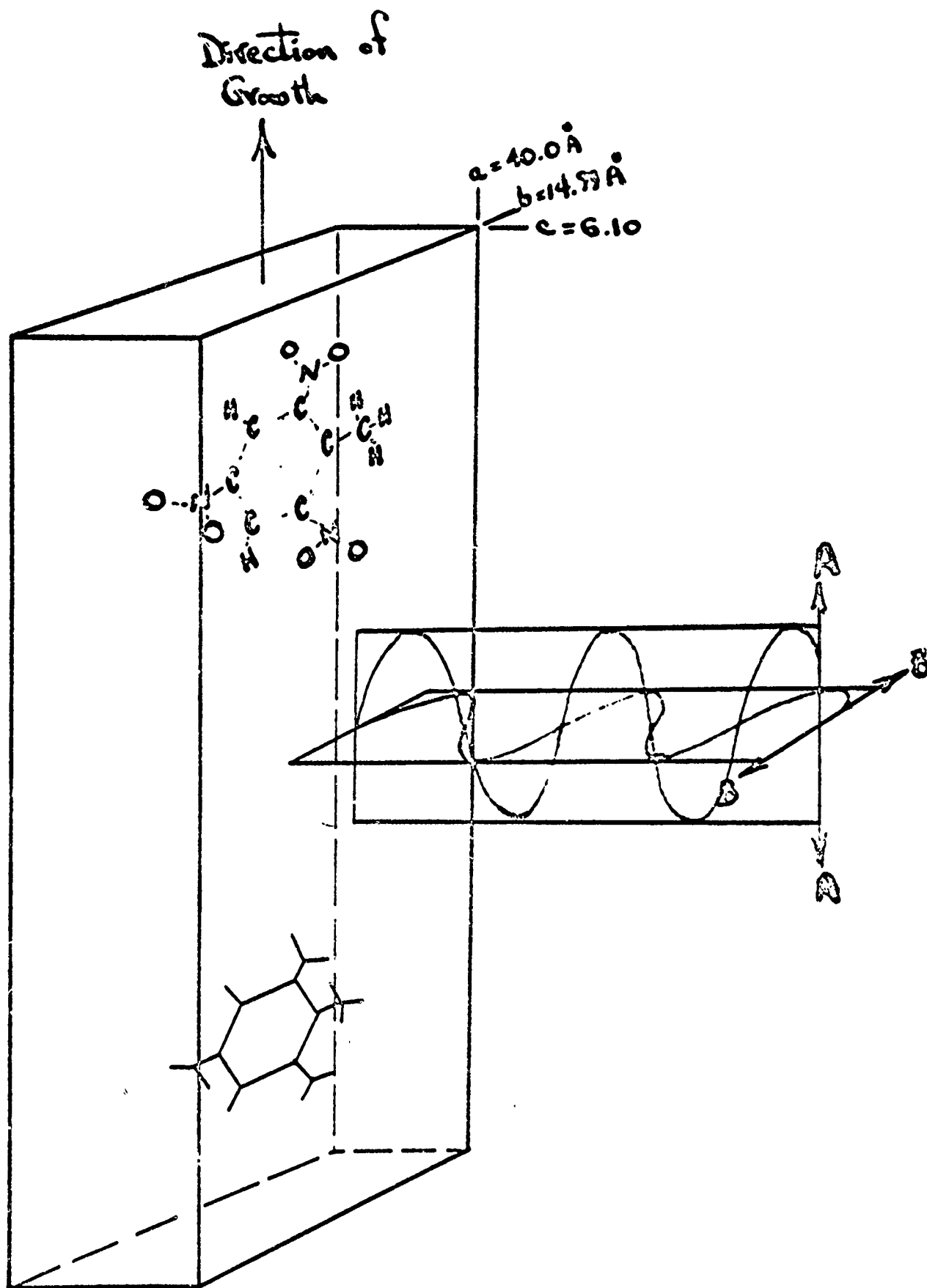


Figure 17. Drawing of single crystal showing orientation of electric vectors for polarized light used to obtain Spectra shown in Figure 16. The resulting orientation of the TNT molecule is shown also.

absorption for one or both azide absorption bands. This might tell, for example, that twice as many azide groups are oriented parallel to the crystallographic a direction as to b or that equal numbers of azide groups are oriented parallel to the three crystallographic axes. Finally, by making the determination quantitative it would be possible to ascertain that all of the azide groups were or were not oriented parallel to the crystallographic axes. This is important because the experimental difficulties increase considerably if the azide groups are wholly or in part oblique to all three crystallographic axes. Quantitative treatment of the data obtained in two views of the crystals will probably eliminate the necessity of preparing a variety of oblique crystal sections.

## II. EXPERIMENTAL APPROACH

The first questions with which we were concerned involve the instrumental parameters. Principally the question arose as to what, if any, polarization is introduced by the spectrophotometer itself. The reflection from aluminized mirrors are believed not to contribute any polarization. Both instruments which we shall use, Perkin-Elmer Model 21 and Model 137, contain a prism as their dispersing element and the prism will introduce a degree of polarization.

Light falling on the prism surface suffers a loss by reflection, and this loss follows the well-known expressions for reflection first given by Fresnel. Fresnel's equations for reflection differ depending on whether the electric vector of the incident light is in, or perpendicular to, the reflecting surface. Using the notation:  $I_0$  = intensity of incident beam,  $I_r$  = intensity of reflected beam,  $i$  = the angle of incidence, and  $r$  = angle of refraction, we can write Fresnel's equations as follows:

$$I_r(\perp) = I_0(\perp) \left[ \frac{\sin^2(r-i)}{\sin^2(r+i)} \right] \quad (1)$$

$$I_r(\parallel) = I_0(\parallel) \left[ \frac{\tan^2(i-r)}{\tan^2(r+i)} \right] \quad (2)$$

The intensity of the transmitted beam ( $I_t$ ) may be obtained by considering the conservation of energy. hence:

$$I_0 = I_r + I_t \quad (3)$$

We may now consider the ratio of the parallel and perpendicular components of the transmitted beam. Combining equations (1), (2) and (3) it can be shown that:

$$I_t(\perp) / I_t(\parallel) = \cos^2(i - r) \quad (4)$$

If this is applied to transmission by a prism at a position of minimum deviation, it can be seen that since only  $i$  and  $r$  are involved in equation (4), each surface will have the same effect; and it follows that for a series of  $n$  prisms the polarization effect is given by

$$[I_t(\perp) / I_t(\parallel)]_n = [\cos(i - r)]^{4n} \quad (5)$$

It is convenient to define the percentage polarization of a beam of light by the expression

$$\%P = 100 \left\{ \frac{1 - I(\perp) / I(\parallel)}{1 + I(\perp) / I(\parallel)} \right\} \quad (6)$$

This can now be applied to the instruments to be used in this investigation. In both Model 21 and 137 the light is twice dispersed by the  $60^\circ$  sodium chloride prism, and therefore it can be calculated that the light is 26.3% polarized. This indicates that light polarized with its vibration direction parallel to the entrance slit will not be transmitted as well by the prism as polarized radiation with its electric vector normal to the entrance slit.

The polarization caused by the prism points out two important points with respect to the design of an appropriate polarizer: (1) It is much more desirable to rotate the sample rather than the polarizer; and (2) The vibration direction is best oriented normally to the entrance slit.

Equation (6) can be rearranged to predict the percentage polarization obtained from a stack of  $m$  parallel plates, having refractive index  $n$ , and oriented at the Brewster angle ( $\tan i = n$ ) with respect to the incident beam, to the following:

$$\%P = 100 m / [m + \{2n / (1 - n^2)\}^2] \quad (7)$$

It is such a stack of plates that is used as the polarizing element.

Silver chloride ( $n_{6\mu} = 1.994$ ) plates are used because of their ease of access and good mechanical properties. The strong dependence of the percentage polarization on refractive index makes materials of high refractive index much more desirable. Selenium films ( $n = 2.56$ ) have been recommended but at the present they are not conveniently

obtainable. Since materials such as selenium films or others may become more available in the future, a flexible design should be sought.

The polarizing attachment illustrated in Figure 18 contains all the essential features that are felt necessary and desirable.

This program like the strain studies in Phase I were seriously hampered by the lack of suitable crystals of  $\alpha$ -PbN<sub>6</sub> and most of the time and effort had to be diverted to the study of crystal growing methods. The fact that good crystals are now being obtained eliminates this problem and we hope to return to this problem soon.

We have recently ordered and expect early delivery of an infrared "microscope" that will enable us to obtain infrared spectra on single crystals less than 0.1 mm in maximum dimension. This is nearly 100X smaller than is normally required. The equipment involved is the microscope attachment for the Model 12-C Perkin-Elmer infrared spectrophotometer. We are looking forward to the application of this instrument to structure problems in general and for the azides, in particular.

### III. CONCLUSION

Although we have made considerable progress this past year on the study of strain and sensitivity we have made a major breakthrough on the problem of growing large clear  $\alpha$ -PbN<sub>6</sub> crystals. With this frustrating problem licked we can proceed with increased hope on the major objectives of this program. We welcome the added tasks of crystal structure determinations for the pseudo stable compounds KN<sub>3</sub>, KO<sub>3</sub> and others related chemically and/or isomorphously.

Respectfully submitted,

  
W. C. McCRONE

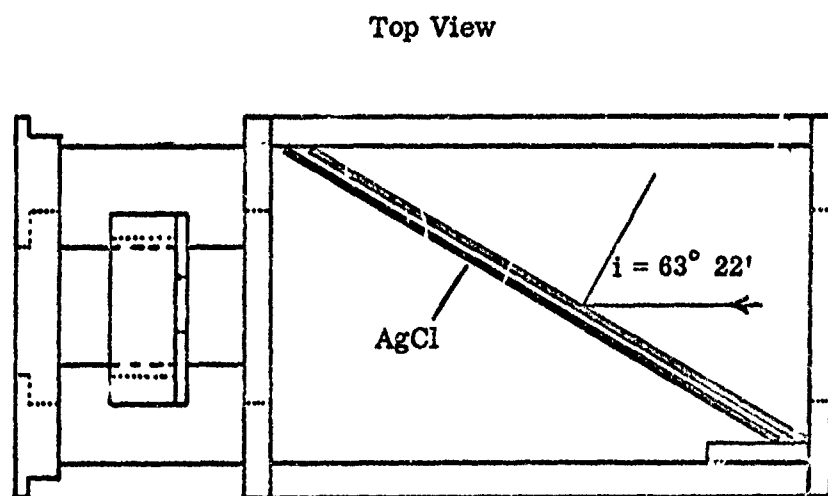
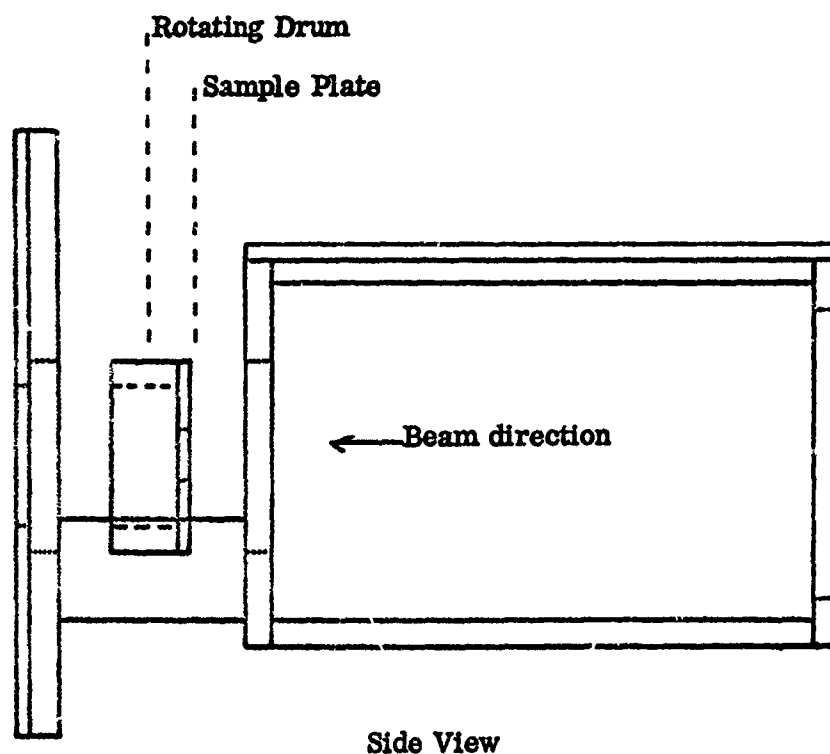


Figure 18. Polarizing attachment for Perkin-Elmer Recording Spectrophotometer

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